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Based on Polyamide**

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the beginning of each regular issue of the PCT Gazette.*

(54) Title: METHOD FOR THE PRODUCTION OF STABILIZED COMPOSITIONS BASED ON POLYAMIDE

(57) Abstract: The invention concerns a method for making stabilised polyamide compositions. The stabilizer is a phosphorous stabilizer selected among phosphorous acid and hyperphosphorous acid. It is introduced before or during polymerisation of the polyamide. The use of said stabilizers enables to avoid foaming phenomena.

## Method for the Production of Stabilized Compositions Based on Polyamide

The invention relates to a process for the production of stabilized compositions based on polyamide and the compositions that can be obtained by means of this process. The compositions according to the invention can be used, in particular, for the production of synthetic threads, fibers and filaments.

Polyamide is a widely used synthetic polymer for the production of threads, fibers and filaments. These fibers, threads and filaments are then used to produce textile surfaces, especially dyed textile surfaces.

Polyamide can suffer degradation when subjected to external elements or conditions, like UV radiation, heat, or bad weather. Degradation can also be induced as a result of the heat used during production and/or molding. This instability is conveyed by way of degradation, loss of mechanical properties, or color changes. These problems can become critical for a certain number of applications.

In order to improve the stability of polyamides it is known to associate additives with them. Numerous additives are marketed for this purpose. They are often classified by their method of action: antioxidant, anti-UV, UV absorbers, etc.

Antioxidants having hindered phenol units, phosphorus stabilizers, light stabilizers having at least one hindered amine unit are known, in particular, for stabilizing polyamide.

Phosphites substituted with alkyl and/aryl radicals, for example tris-(2,4-di-tert-butyl-phenyl) phosphite are known for stabilization. These stabilizers, when introduced to the preparation medium of a polyamide, cause strong foaming which runs the risk of affecting the equipment and the produced products. This strong foaming even occurs in the presence of conventional antifoaming agents. In order to avoid this problem, document WO 9418364 teaches the introduction of these stabilizers by mixing [*them in*]<sup>1</sup> in the molten polyamide phase and with a masterbatch of stabilizer in a polyamide matrix.

Foaming problems can also be encountered with other stabilization additives.

For different reasons of a technical or economic nature, it is often preferable to introduce additives to a polymer other than by being mixed into the molten phase. Thus, an introduction of

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<sup>1</sup> **Translator's Note:** italicized text in square brackets is not present in the French source text, but implied and sometimes needed in order to make the English read more appropriately.

additives to the synthesis medium of the polymer before polymerization is often preferred. This introduction process is generally summarized under the term "introduction to synthesis". This type of process, among other things, permits a very good dispersion of the additives in the polymer and sometimes avoids operations to remelt the polymer. In addition, an introduction of stabilizers to the synthesis [*medium*] avoids degradation during the production of the polyamide and/or its molding.

The purpose of the invention is to propose a process for the production of a stabilized composition based on a polyamide containing an additive based on phosphorus introduced to the synthesis [*medium*].

For this purpose, the invention proposes a production process of a stabilized composition based on polyamide, containing a phosphorus stabilization additive, characterized by the fact that the phosphorus stabilization additive is chosen from phosphorous acid and hypophosphorous acid and by the fact that it is introduced to the polymerization medium of the polyamide before or during the polymerization phase. The weight amount in the composition is preferably between 0.01 and 0.04%.

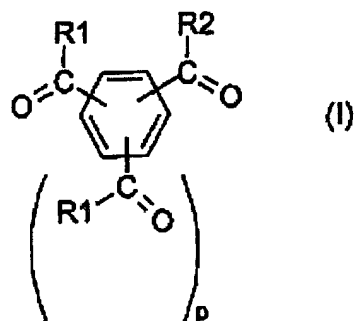
According to a preferred embodiment, at least one other stabilization additive can be used, being introduced to the polyamide polymerization medium before or during the polymerization phase. The additional additive is chosen among hindered phenol antioxidants and light stabilizers having at least one hindered amine group (Hindered Amine Light Stabilizer H.A.L.S.). A combination of these two additives with the phosphorus stabilizer could also be used. The presence of the phosphorus stabilizer chosen from phosphorous acid and hypophosphorous acid also permits a reduction in the foaming due to the additional additives.

Light stabilizers having at least one hindered amine unit improve the light stability of polyamide and avoid the loss of color brightness when the polyamide is dyed or contains colored pigments.

The polyamide production process according to the invention can be chosen from all known processes, provided that the phosphorus stabilizer and, if necessary, the other stabilization additives, are introduced to the polymerization medium before the polymerization phase has actually begun. It is possible for a product having a limited degree of polycondensation to be formed before the introduction of the additives.

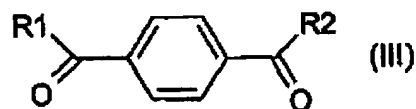
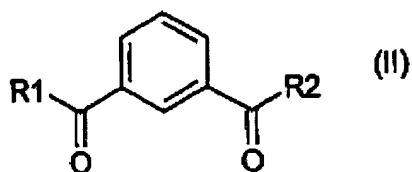
In the event that several stabilization additives are used, these can be introduced to the polymerization medium either successively, at different stages of the process before the polymerization phase, or at the same time.

The light stabilizer having at least one hindered amine group is preferably chosen from 4-amino-2,2,6,6-tetramethylpiperidine, 4-carboxy-2,2,6,6-tetramethylpiperidine, aromatic compounds of formula (I) containing two or three carbonyl functions and containing at least one group having a hindered amine unit, this unit being contained in a group bonded to one of the carbonyl functions. The carbonyl function can be contained in an amide, ester or ester-amide group



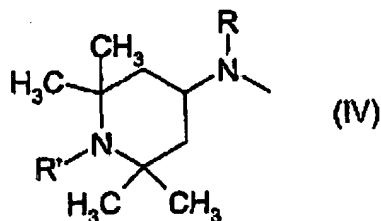
where p is equal to 0 or 1, and R1 and R2 are identical or different groups, at least one of which has a hindered amine unit.

If p is equal to 0, the additive can have a chemical structure (II) or (III) defined as follows:



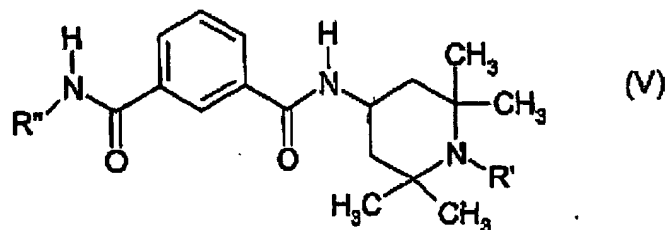
where R1 and R2 are identical or different groups, at least one of which has a hindered amine unit, a group not containing a sterically hindered amine unit that can be chosen from C<sub>1</sub> to C<sub>18</sub> alkoxy; aminoalkyls optionally substituted with hydrogen, C<sub>1</sub> to C<sub>5</sub> alkoxy, carbonyl groups, carbamyl groups or alkoxy carbonyl groups; C<sub>3</sub> to C<sub>5</sub> epoxides;

The group or groups containing a sterically hindered amine unit can be chosen from compounds of the following formula (IV):



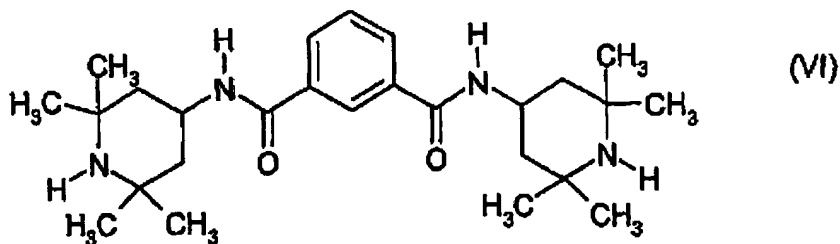
where R and R' are independently chosen from hydrogen, C<sub>1</sub> to C<sub>12</sub> alkyls, C<sub>1</sub> to C<sub>8</sub> alkoxy, groups with the structure -COR<sub>3</sub>, where R<sub>3</sub> is chosen from hydrogen, C<sub>1</sub> to C<sub>6</sub> alkyls; phenyl; the -COO group (C<sub>1</sub> to C<sub>4</sub> alkyl); the group with the structure NR<sub>5</sub>R<sub>6</sub>, where R<sub>5</sub> and R<sub>6</sub> are chosen independently from hydrogen, C<sub>1</sub> to C<sub>12</sub> alkyls, C<sub>5</sub> or C<sub>6</sub> cycloalkyls, phenyl, alkylphenyl in which the alkyl is C<sub>1</sub> to C<sub>12</sub>, where R<sub>5</sub> and R<sub>6</sub> form a ring with 5 to 7 atoms with the nitrogen atom to which they are bonded, optionally containing an oxygen atom or another nitrogen, preferably forming a group of the piperidine or morpholine family.

A preferred compound for light stabilization is the compound of formula (V):



where R'' is chosen from C<sub>1</sub> to C<sub>20</sub> alkyls, C<sub>1</sub> to C<sub>20</sub> aminoalkyls, C<sub>1</sub> to C<sub>20</sub> substituted aminoalkyls, C<sub>1</sub> to C<sub>20</sub> hydroxyalkyls, C<sub>1</sub> to C<sub>20</sub> alkenes, C<sub>1</sub> to C<sub>20</sub> substituted alkenes, alkoxyalkyl groups, C<sub>1-20</sub>-oxy-N-C<sub>1-20</sub> alkyl groups, C<sub>1</sub> to C<sub>10</sub> N-cycloalkyl groups, C<sub>1</sub> to C<sub>10</sub> N-cycloalkyl groups substituted with a -COR<sub>4</sub> groups where R<sub>4</sub> is chosen from hydrogen, C<sub>1</sub> to C<sub>6</sub> alkyls, phenyl, the groups C<sub>1-20</sub>COO(H or C<sub>1-4</sub> alkyl) and where R' has the same meaning as for formula (IV).

The light stabilizer is even more preferably the compound of formula (VI)



This additive, for example, is furnished by the Clariant Co. under the name Nylostab S-EED.

The amount of light stabilization additive in the composition is advantageously between 0.15 and 0.5 wt%.

The light stabilizer of formula (VI) is preferably introduced to the polymerization medium in the form of a suspension or a solution in water, caprolactam, or a mixture of water and caprolactam. The weight concentration in the solution or suspension can be between 5 and 50%. A mixture of caprolactam and water containing more caprolactam than water is preferred. The form of introduction, suspension or solution, can depend in part on the temperature and pressure conditions during introduction.

The antioxidant is preferably chosen from alkylated monophenols, alkylated hydroxy-quinones, alkylidene bisphenols, benzyl compounds with alkyl hindrance, acylaminophenols,  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid esters. One can mention, in particular, 1,3,5-trimethyl-2,4,6-tris(3,5-tert-butyl-4-hydroxybenzyl)benzene, for example furnished by the Ciba Co. under the name IRGANOX 1330 and N,N'-hexamethylene bis(3,5-tert-butyl-4-hydroxy-hydrocinnamamide), for example, supplied by the Ciba Co under the name IRGANOX 1098.

The amount of the second additive in the composition is advantageously between 0.10 and 0.30 wt%.

The stabilized composition based on polyamide can contain other additives in addition to the additives already mentioned. These additives can be introduced by mixing with the polymerization medium or by being mixed into the molten phase. As examples of such additives one can mention pigments or matting agents intended to impart a mat and/or colored appearance to the compositions, fire retardants, other stabilizers.

According to a particular embodiment of the invention, the compositions contain a matting agent in the form of particles based on titanium dioxide or zinc sulfide. The concentration of particles in the composition can be between 0.01 and 3 wt%. It is advantageously greater than 1%. The matting agent is preferably introduced to the polymerization medium before and during the polymerization phase. According to this embodiment, the particles are advantageously introduced in the form of an aqueous suspension. The particles based on titanium oxide are advantageously coated. This can involve, for example, a coating based on silica with alumina and/or manganese oxide, if necessary.

The composition produced by the process according to the invention can be based on a polyamide of the type obtained by means of polymerization from a lactam and/or an amino acid, or based on a polyamide of the type obtained as a result of the polycondensation of a carboxylic diacid and a diamine. The compositions are preferably based on polyamide 6, polyamide 66, mixtures and copolymers based on polyamides. In particular, they can be a polyamide 6.6/6 copolymer if a stabilizer of formula (VI) is used, introduced to the polymerization medium in the form of a solution and dispersion in a liquid containing caprolactam.

According to a particular embodiment, the composition is based on polyamide 6.6. An advantageous production process uses as the raw material a hexamethylenediammonium adipate salt, preferably in the form of a solution with a salt concentration between 50 and 70 wt%. This continuous or batch process includes a first water evaporation phase and a second polymerization phase by means of polycondensation.

The compositions can be formed into threads, fibers and filaments directly after polymerization without intermediate steps of solidification and remelting. They can also be formed into granules intended to undergo remelting to then be definitively formed, for example, for the production of molded articles or the production of threads, fibers or filaments.

The threads, fibers and filaments formed from the compositions obtained as a result of the process according to the invention are produced by means of melt spinning: the composition is extruded in the molten state through spinnerets containing one or more openings.

All melt spinning processes can be used. The filaments can be drawn in the form of a multifilament thread or sliver in a continuous step or with repetition and undergo different treatments: sizing, texturing, fixation, etc.

For the production of multifilament threads one can mention in particular the high-speed spinning process with spinning rates of greater than 3500 m/min. Such processes are often denoted with the following terms: POY (partially oriented yarn), FOY (fully oriented yarn), FEI (spinning-drawing-integrated). These threads can also be textured according to the use for which they are intended. The threads obtained as a result of these methods are particularly suited for the production of woven or knitted textile surfaces.

For the production of fibers, the filaments can be combined in the form of a sliver or lap directly after spinning or can be repeatedly drawn, textured and cut. The obtained fibers can be used for the production of nonwovens or fiber yarns.



The composition can also be used for the production of flock.

The threads, fibers and filaments and articles obtained from the threads, fibers and filaments can be dyed. One can mention in particular vat dyeing or dyeing with jets. The preferred dyes are acid, metalliferous or nonmetalliferous dyes.

The compositions according to the invention permit particles to be produced whose dyeing behavior in light is excellent. They also permit better wash-fastness of dyes to be obtained.

Other details or advantages of the invention will be more clearly apparent by means of the following examples provided only as indication.

#### Example 1

A copolymer based on polyamide 66 is produced from 3,590 kg in an aqueous solution of hexamethylenediammonium adipate salt concentrated to 62% by weight and to which the following are added:

- 3,940 g of an aqueous solution of 25% acetic acid
- 1,000 g of an aqueous solution of 40% phosphorous acid
- 300 g of Rhodia Silcolapse 5010 antifoaming agent
- a dispersion [*obtained*] by mixing of 40 L of caprolactam, 10 L of water, 6 kg of Nylostab SEED marketed by the Clariant Co., [*and*] 3 kg of Irganox 1098 marketed by the Ciba Co.

The polyamide is produced according to a standard process comprising a stage for the concentration of the solution in an evaporator, a polycondensation stage in a stirred autoclave reactor with a phase of about 45 minutes of distillation under a pressure stage of 1.85 MPa for which the final temperature is 245°C, a phase of about 35 minutes of decompression from 1.85 MPa to 0.1 MPa at a final temperature of 260°C and a finishing phase of about 30 minutes for which the final temperature is 270°C.

During the pressure distillation phase, after 6 minutes, 128 kg of a 25wt% aqueous dispersion of coated titanium dioxide particles is added.

No foaming is observed during the decompression phase. A copolymer based on polyamide 6.6 is obtained containing 2.0 wt% of polyamide 6 units and 1.6% of titanium dioxide.

The copolyamide is spun according to a spinning-drying-integrated process. The winding rate is 4500 m/min. The titer of the obtained threads is 78 dtex for 68 filaments. The thread tenacity is 42 cN/tex and the elongation at break is 38%.

A knitted surface is produced from the threads. The surface is washed at 60°C for 20 minutes in the presence of a detergent composition consisting of 2 g/L of Sandozine MRN marketed by the Clariant Co., 2 g/L of Sirrix AR and 2 g/L of sodium carbonate. The surface is then heat-fixed at 190°C for 45 seconds.

The surface is dyed by dipping at 98°C for 45 minutes at pH 6 in the presence of the following agents:

- dyeing agents marketed by the Ciba Co.
  - 0.0247 wt% of Irgalanyellow 3 RV 250%
  - 0.0170 wt% of Irgalanbordo EL 200%
  - 0.2220 wt% of Irgalangray 200%
- 2 wt% of a Unisson C14 agent marketed by the CHT Co.
- 0.5 g/L of sodium acetate

The light-fastness of the surface was tested with a Xenotest 450 apparatus according to standard DIN 75202 over four cycles (FAKRA test). After four cycles the score is 6 to 7.

#### Example 2 (comparative)

A copolyamide is produced according to the process of example 1 without dissolution of phosphorous acid or the mixture caprolactam + water + Nylostab + Irganox. The score is 5.

#### Example 3

Compositions based on polyamide 6.6 are prepared in a 300 mL reactor equipped with a view port that permits observation of any foaming. The polyamide is prepared from a hexamethylenediammonium adipate salt in solution according to a process related to that of example 1. The decomposition phase is accomplished in 10 minutes so that conditions close to the conditions of example 1 are obtained in terms of foaming sensitivity. During preparation the following additives are added:

- Coated titanium dioxide particles (1.6 wt% relative to the obtained composition). The particles are added 5 minutes after the beginning of the plateau at 1.85 MPa.
- Phosphorous acid in solution: added to the hexamethylenediammonium adipate salt solution.
- Nylostab SEED marketed by the Clariant Co., Irganox 1098, Irgafos 168 (phosphorus stabilizer), Irgafos 12 (phosphorus stabilizer), marketed by the Ciba Co. These products are introduced to the molten caprolactam at 150°C during the decompression phase.

Different additives as well as different combinations are tested. The results are shown in Table 1.

**Table 1**

Irganox 198	Irgafos 168	Irgafos 12	H <sub>3</sub> PO <sub>3</sub>	Nylostab	Foaming level
0.15%	/	/	/	/	1
/	0.15%	/	/	/	1
/	/	/	/	0.3%	1
0.15%	/	0.15%	/	0.3%	3
0.15%	/	/	0.02%	0.3%	0

The amounts of additives are expressed in weight relative to the obtained composition. The foaming level is evaluated by the foam height in the reactor: 0 for low foaming, 3 for very substantial foaming.

It is observed that phosphorous acid inhibits foaming induced by the presence of the other additives.

### Claims

1. A method for the production of a stabilized composition based on polyamide containing a phosphorus stabilization additive, characterized by the fact that the phosphorus stabilization additive is chosen from phosphorous acid and hypophosphorous acid and by the fact that it is introduced to the polyamide polymerization medium before or during the polymerization phase.

2. The method according to Claim 1, characterized by the fact that the composition contains at least one other stabilization additive introduced to the polyamide polymerization medium before or during the polymerization phase chosen from hindered phenolic antioxidants and light stabilizers having at least one hindered amine unit.

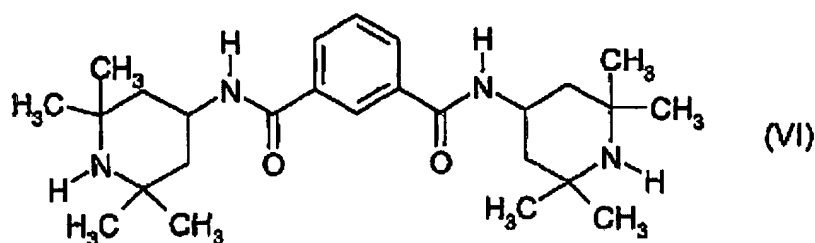
3. The method according to one of the preceding claims, characterized by the fact that the composition contains as other stabilization additive:

- an antioxidant chosen from alkylated monophenols, alkylated hydroxyquinones, alkylidene bisphenols, benzyl compounds with alkyl hindrance, acylaminophenols,  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid

and/or

- a light stabilizer having at least one hindered amine unit chosen from aromatic compounds containing two or three carbonyl functions to which at least one sterically hindered amine unit is attached, said unit being in a group bonded to one of the carbonyl functions, 4-amino-2,2,6,6-tetramethylpiperidine, 4-carboxy-2,2,6,6-tetramethylpiperidine.

4. The method according to Claim 3, characterized by the fact that the light stabilizer having at least one hindered amine unit is the compound of formula (VI)



5. The method according to one of the preceding claims, characterized by the fact that the composition contains particles based on titanium oxide introduced before the polyamide polymerization phase.

6. The method according to Claim 5, characterized by the fact that the weight amount of particles based on titanium dioxide is greater than 1 wt% relative to the weight of the composition.

7. The method according to one of the Claims 5 or 6, characterized by the fact that the particles based on titanium dioxide are coated.

8. The method according to one of Claims 4 to 7, characterized by the fact that the light stabilizer having at least one hindered amine unit is introduced in solution or suspension in a liquid chosen from water, caprolactam and their mixtures.

9. The method according to one of the preceding claims, characterized by the fact that the polyamide is chosen from polyamide 6, polyamide 6.6 and their copolymers.

10. The method according to Claim 8, characterized by the fact that the polyamide is polyamide 6.6 produced from a solution in water of hexamethylenediammonium adipate, the method including a water evaporation phase then a polycondensation phase, the solution or suspension of light stabilizer having a hindered amine unit being introduced before the evaporation stage.

11. The method according to one of the preceding claims, characterized by the fact that it is a batch method for the production of a composition based on polyamide 6.6.
12. A composition based on polyamide capable of being prepared by means of a method according to one of the preceding claims.
13. The composition according to Claim 12, characterized by the fact that it contains 0.01 to 0.04 wt% of additive chosen from phosphorous acid and hypophosphorous acid.
14. The composition according to one of the preceding claims, characterized by the fact that it contains 0.15 to 0.5% of light stabilizer having at least one hindered amine unit and 0.10 to 0.30 wt% of a hindered phenolic antioxidant.
15. The composition according to one of the Claims 12 to 14, characterized by the fact that it contains particles based on titanium dioxide.
16. The composition according to Claim 15, characterized by the fact that the particles based on titanium dioxide are coated.
17. Threads, fibers and filaments obtained by means of molding a composition according to one of the Claims 12 to 16.
18. Woven, knitted, nonwoven or flocked, dyed articles obtained from threads, fibers and filaments according to Claim 17.